

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Improvements in Hydroforming

We, BASS RESEARCH AND ENGINEERING COMPANY, formerly known as Standard Oil Development Company, a corporation duly organized and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the catalytic conversion of hydrocarbon fractions boiling within the motor fuel boiling range of low knock rating into high octane number motor fuels rich in aromatics and particularly to a process whereby such a conversion is effected by the fluidized solids technique.

Hydroforming is a well known and widely used process for treating hydrocarbon fractions boiling within the motor fuel or naphtha range to upgrade the same or increase the aromaticity and improve the anti-knock characteristics of said hydrocarbon fractions. By hydroforming is ordinarily meant an operation conducted at elevated temperatures and pressures in the presence of solid catalyst particles and hydrogen whereby the hydrocarbon fraction is increased in aromaticity and in which operation there is no net consumption of hydrogen. Hydroforming operations are ordinarily carried out in the presence of hydrogen or a hydrogen rich recycle gas at temperatures of 750–1150° F. in the pressure range of about 50–1000 lbs. per sq. inch and in contact with such catalysts as molybdenum oxide, chromium oxide, or, in general, oxides or sulfides of metals of Groups IV, V, VI, VII and VIII of the Periodic System of elements, alone or generally supported on a base or spacing agent such as alumina gel, precipitated alumina or zinc aluminate spinel. A good hydroforming catalyst is one containing about 10 wt. per cent molybdenum oxide upon an aluminum oxide base prepared by heat treat-

ing a hydrated aluminum oxide or upon zinc ammoniate spinel.

It has been proposed to effect the hydroforming of naphtha fractions in a fluidized solids reactor system at elevated pressures in which naphtha vapors are passed continuously in admixture with a hydrogen-rich gas through a dense fluidized bed of hydroforming catalyst particles in a reaction zone, spent catalyst particles are withdrawn from the dense bed in the reaction zone and passed to a separate regeneration zone where inactivating carbonaceous deposits are removed by combustion whereupon the regenerated catalyst particles are returned to the main reactor vessel or hydroforming reaction zone. Fluid hydroforming as thus conducted has several fundamental advantages over fixed bed hydroforming, such as, (1) the operations are continuous (2) the vessels and equipment can be designed for single rather than dual functions, (3) the reactor temperature is substantially constant, and, (4) the regeneration or reconditioning of the catalyst may be readily controlled. Attention is drawn to our prior British Patents 706,938 and 723,491 which cover features of fluid hydroforming.

It has been proposed in connection with said fluidized solids operation to strip the spent catalyst with steam or an inert gas such as nitrogen, flue gas or the like prior to charging the spent catalyst to the regenerator and to strip the regenerated catalyst with the same stripping gases prior to recycling the regenerated catalyst to the reaction zone.

It has been found that the presence of relatively small amounts of carbon monoxide and/or carbon dioxide in the reaction zone results in a considerable loss in activity and selectivity of the catalyst. For example, the inclusion of 3–4 volume % of carbon monoxide base on the inlet hydrogen to a hydroforming unit reduced the Research Octane number of the C₈–430° F. product from 91 to 89 and 90

increased the carbon yield from 0.4 to 0.9 wt. % at 90 Research Octane number, while the presence of 1-2 vol. % of carbon dioxide based on the inlet hydrogen reduced the

5 Research Octane number of the C_{12} -430° F. product from 91 to 87 and increased carbon yield from 0.4 to 0.5 wt. % at 90 Research Octane number.

Also encountered in carrying out a hydro-
10 forming reaction is that the metal oxide catalysts, particularly those of molybdenum, slowly lose activity under normal regenerating and reaction conditions. This does not involve a residual carbon deposition of catalyst, but
15 rather a valence or crystal structure condition of the metal oxide itself. Modern catalyst theory now indicates that the activity of the catalyst depends upon the strain in the crystal structure. Apparently with the metal oxide
20 catalysts this necessary strained condition of the crystals is slowly lost during the alternating oxidation and reduction of the operation. Thus, for example, in the case of molybdena, the reduction of the catalyst at temperatures
25 of 1000° F. or higher in the presence of small concentrations of moisture, which evolve from the reduction of the oxidized catalyst, results in a measurable growth of crystals larger than 50A. The same crystal growth has been noted
30 in the reactor, for as yet unknown reasons. This growth of crystals has resulted in a loss of activity and selectivity in the hydroforming reaction.

It is an object of this invention to provide
35 the art with an improved procedure for stripping regenerated hydroforming catalyst particles free from carbon monoxide and carbon dioxide and also destroying the large crystals and obtaining the desired crystal structure
40 strain.

The present invention is a process for hydro-
forming by the fluidized solids technique in which the freshly regenerated catalyst particles are stripped with air, and the air stripped
45 stream of catalyst purged with nitrogen or flue gas before recycling to the reaction zone.

The air-stripped regenerated catalyst is preferably treated in the regenerated catalyst
standpipe with nitrogen, or flue gas which has
50 been scrubbed free of oxygen and carbon oxides, in a small amount sufficient to displace or purge the oxygen entrained in the stripped regenerated catalyst from the latter. The stripped and purged catalyst is then in
55 good condition for recycling to the reactor by way of a short time, high temperature hydrogen pretreatment, by way of a low temperature, long time hydrogen pretreatment or, as has more recently been found, the stripped and
60 purged regenerated catalyst may be added directly to the reaction zone without pretreatment.

The carbon oxides and water vapor entrained with the regenerated catalyst entering
65 an air stripper could be readily removed

by the introduction of about 2 V/V of air to the stripper. However, in order to remove the adsorbed carbon oxides and water, additional stripping air is required say up to about 5 V/V. It is preferred to employ about 2-5 minutes
70 holding time in the air stripper in order to provide sufficient holding time at the low carbon oxides and water partial pressures to permit adequate desorption of the carbon oxides and water which are detrimental to the
75 hydroforming reaction.

The air-stripped catalyst may pass from the bottom of the stripper into a conduit which forms a standpipe for developing the
fluidstatic pressure necessary to overcome the
80 pressure drop encountered in the transfer of regenerated catalyst back into the reactor. Since some air will be carried into the standpipe by the air-stripped catalyst it is necessary to strip or purge the stream of catalyst to free it
85 of air before recycling the catalyst to the reactor. This may be done by adding nitrogen or flue gas that has been scrubbed free of oxygen and carbon oxides at one or more points along the stand-
90 pipe. Only relatively small amounts of nitrogen are required to purge oxygen from the catalyst in the standpipe because of the higher density of the catalyst and because of the high
L/D of the standpipe. The amount of nitrogen
95 or scrubbed flue gas thus added is very small (about 0.09 to 0.2 SCFH/lb. of catalyst circulated) and serves merely to reduce the amount of oxygen entrained with the catalyst to less than one part in 20,000.

The air-stripped and nitrogen purged
100 regenerated catalyst may be handled in a variety of ways. It may, for example, be recycled directly to the reactor without pretreatment, or it may be discharged into a
105 stream of hot hydrogen-rich recycle gas which serves to pretreat the catalyst and at least partially reduce higher catalytic oxides formed during regeneration into a lower or more active form of catalytic metal oxide. Since the regenerated catalyst is hot (1050-1200° F.) and the recycle or hydrogen-rich gas is at
110 about 1100-1200° F. the pretreatment of hot regenerated catalyst must not be continued for more than a few seconds, generally less than 10 and preferably less than 5 seconds in order
115 to prevent overtreating and/or thermal degradation of the catalyst. While the entire mixture of catalyst and pretreating gas may be discharged directly into the reactor bed it is
120 advantageous to separate the regenerated and pretreated catalyst from the pretreating gas as quickly as possible and to by-pass the pretreating gas around the main reactor bed. The
stripped and purged regenerated catalyst may
125 also be given a pretreatment at lower temperatures for longer periods of time in various ways. A particularly advantageous operation of the latter type is illustrated in the drawing.

The feed or charging stock to the hydro- 130

forming reactor may be a virgin naphtha, a cracked naphtha, a Fischer-Tropsch naphtha or the like. The feed stock is preheated alone or in admixture with recycle gas to reaction temperature or to the maximum temperature possible while avoiding thermal degradation of the feed stock. Ordinarily preheating of the feed stock is carried out to temperatures of about 800—1050° F., preferably about 1000° F. The naphtha preheat should be as high as possible while avoiding thermal degradation thereof as by limiting the time of residence in the furnace and the transfer or feed inlet lines. The preheated feed stock may be supplied to the reaction vessel in admixture with hydrogen-rich recycle gas or it may be introduced separately as shown. The recycle gas, which contains from about 50 to 70 vol. per cent. hydrogen is preheated to temperatures of about 1100—1300° F. prior to the introduction thereof into inlet line 12. The major proportion (at least 85%) of the recycle gas is introduced directly into the bottom of reactor vessel 10 while a minor proportion only (at most about 15%) is introduced into reactor catalyst recycle line or into the riser line 47. The recycle gas should be circulated through the reactor at a rate of from about 1000 to 8000, preferably about 4000 cu. ft. per bbl. of naphtha feed.

The reactor system is charged with a mass of finely divided hydroforming catalyst particles. Suitable catalysts include Group VII metal oxides, such as molybdenum oxide, chromium oxide or tungsten oxide of mixtures thereof upon a carrier such as activated alumina, zinc aluminate spinel or the like. Preferred catalysts contain about 5 to 15 wt. molybdenum oxide or from about 10 to 40 wt. % chromium oxide upon a suitable carrier. If desired minor amounts of stabilizers and promoters such as silica, calcium oxide, ceria or potassia can be included in the catalyst. The catalyst particles are, for the most part between 200 and 400 mesh per linear inch in size or about 0—200 microns in diameter with a major proportion between 20 and 80 microns.

The hydroforming reactor vessel should be operated at temperatures between about 850 and 950° F., preferably about 900° F. and at pressures between 50 and 500 lbs. per sq. inch preferably about 200 lbs. per sq. inch. Temperatures above 900° F. result in increased carbon formation and lower selectivity to gasoline fractions while at temperatures below about 900° F. operating severity is low and would therefore require an excessively large reaction vessel. Lowering reactor pressure below 200 lbs. per sq. inch ordinarily results in increased carbon formation which becomes excessive in most cases at pressures below about 75 lbs. per sq. inch. Above 200 lbs. however, catalyst selectivity to light products (C₄'s and lighter) increases rapidly. The regenerator is operated at essentially the same

pressure as the reactor and at temperatures of about 1050—1300° F. The residence time of the catalyst in the reactor may be of the order of 3 to 4 hours while the residence time of the catalyst in the regenerator may be from about 3 to 15 minutes. The superficial velocity of the gaseous or vaporous materials through the reaction and regeneration zones is about 0.2 to 0.9 ft. per second.

In the stripper good results are achieved by contacting the catalyst at temperatures of from about 1050 to 1200° F., during a time period of from about 3—300 seconds using 1 to 50 standard cubic feet of air per pound of catalyst. Enough nitrogen is then passed through the stripper to dislodge the oxygen before delivery of the catalyst to the reactor. The catalyst may be treated with hydrogen at 900—1250° F. for 2 to 100 seconds with that amount of hydrogen which is equal to 75—200% if the theoretical amount necessary to lower the valency of the oxide catalyst one number, before delivery to the reactor.

The weight ratio of catalyst to oil introduced into the reactor should be about 0.5 to 1.5. It is preferred to operate at catalyst to oil ratios of about 1 since ratios above about 1 to 1.5 result in excessive carbon formation. Somewhat higher weight ratios can be used at higher pressures.

Space velocity or the weight in pounds of feed charged per hour per pound of catalyst in the reactor depends upon the age or activity level of the catalyst, the character of the feed stock and the desired octane number of the product. Space velocity for a molybdenum oxide on alumina gel catalyst may vary, for example, from about 1.5 wt./hr./wt. to about 0.15 wt./hr./wt.

In our prior British Patent 730,223 there is described and claimed a process of hydroforming hydrocarbons in contact with fluidized finely divided hydroforming catalyst particles which comprises continuously withdrawing a stream of catalyst particles from a reaction zone, regenerating the withdrawn catalyst particles by burning carbonaceous deposits therefrom at elevated temperatures, withdrawing a stream of regenerated catalyst particles from the regeneration zone, withdrawing a second stream of catalyst particles from the reaction zone, cooling the stream of hot freshly regenerated catalyst particles with said second stream of reactor catalyst particles treating the cooled freshly regenerated catalyst with hydrogen-rich gas and recycling the hydrogen treated regenerated catalyst particles to the reaction zone. Claim is not made herein to a process of hydroforming in which a stream of hot freshly regenerated catalyst particles is cooled with a stream of reactor catalyst particles.

Subject to the above disclaimer what we claim is:—

1. A process for hydroforming hydrocar-

- bons in contact with finely divided hydroforming catalyst particles in accordance with the fluidized solids technique in which a stream of spent catalyst particles is continuously withdrawn from the reaction zone and regenerated by burning carbonaceous deposits therefrom in a regeneration zone and in which a stream of regenerated catalyst is withdrawn from the regeneration zone, stripped with air, the air-stripped stream of catalyst being purged with nitrogen or flue gas scrubbed free of oxygen and carbon oxides, and in which the regenerated catalyst particles are recycled to the reaction zone.
- 15 2. A process according to Claim 1 in which the spent catalyst particles are withdrawn from a dense fluidized bed in the reaction zone, in which the regeneration zone is separate, in which regenerated catalyst particles are withdrawn from a dense fluidized bed in the regeneration zone, and in which the air-stripped regenerated catalyst particles are compacted, but still retained in a fluidized condition, by passing to a downwardly moving column of
- 25 air-stripped regenerated catalyst particles, the compacted column of catalyst particles being contacted with nitrogen to purge them of entrained oxygen and thereafter recycled to the reaction zone.
- 30 3. A process according to Claim 1 or Claim 2 in which the purged regenerated catalyst particles are contacted with a hydrogen-containing gas and in which the particles so contacted are recycled to the reaction zone.
- 35 4. A process as claimed in Claim 3 in which the contacting with hydrogen-containing gas is effected at substantially regenerator temperature for less than 10 seconds.
5. A process as claimed in Claims 3 or 4 in which the contacting of the purged regenerated catalyst particles with a hydrogen-containing gas is effected at temperatures approaching reactor bed temperatures for a period sufficient to reduce higher catalytic metal oxides formed during regeneration to a lower, more catalytically active form of catalytic metal oxide.
6. A process as claimed in any of Claims 3 to 5 in which the contacting with a hydrogen-containing gas of the regenerated catalyst is effected immediately prior to recycling the catalyst to the reaction zone, in a separate pre-treatment zone with a hydrogen-containing gas at a temperature in the range of 900° to 1250° F. for a time interval of 2 to 100 seconds with an amount of hydrogen equal to 75—200% of the theoretical for one valence change in order to convert the higher catalytic metal oxide into a lower more catalytically active form.
7. A process as claimed in any of Claims 1 to 6 in which the hydroforming catalyst comprises a Group VI metal oxide upon a support.
8. A process as claimed in any of Claims 1 to 7 in which the regenerated catalyst particles are stripped with air at 1100° to 1200° F.
9. A process for hydroforming substantially as hereinbefore described.

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767605 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale.

